AADE 01-NC-HO-11

Can Synthetic-Based Muds Be Designed to Enhance Soil Quality?

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Abstract

An invert emulsion drilling fluid has been developed that possesses the drilling properties of conventional invert muds but which can be discharged (as mud-coated drilled cuttings) onto land as a soil enhancer. The individual components of this drilling fluid – base fluid, internal polar phase, emulsion stabilizers, wetting agents, fluid-loss reducing agents and weighting material -- also possess these attractive features.

One version of this drilling fluid is designed to be rapidly land farmed (without pretreatment of the drill cuttings) in areas where government regulations permit and receiving environment conditions are appropriate. For areas where direct application of drilled cuttings is severely restricted, another version of the drilling fluid can be used in conjunction with rapid bioremediation or other pre-treatment. For example, the Louisiana 29-B regulations place stringent restrictions on the composition of soil/waste mixtures, which include limitations on electrical conductivity and residual oil and grease.

Introduction

Development of Synthetic-Based Muds (SBM) as alternatives to conventional oil-based muds (OBM) in offshore operations was precipitated by toxicity and biodegradability concerns. These focused on the fate and effects of mud-laden drilled cuttings discharged into the sea, as well as worker safety. For onshore applications, cuttings disposal is also of paramount importance. However, since the drilled cuttings are disposed of on land, the environmental issues focus primarily on usability of that land and contamination of ground water[1,2] with chloride salts and hydrocarbons. Although the advent of SBM has greatly improved the environmental acceptability of non-aqueous drilling fluids both offshore and onshore, current SBM formulations still present problems for direct land treatment of mud-laden cuttings in onshore operations. The concerns with pollution of soil and groundwater by SBM and OBM have led to increasingly strict government regulations.

In addition to land treatment (spreading and farming), there is a litany of other ways to deal with invert mud-laden cuttings in onshore drilling operations.[3] These include landfill disposal; bioremediation (composting and bioreacting); stabilization/solidification (briquetting, fixation with silicates or fly ash); extraction or washing (oil, detergents, and solvents); and thermal treatment (incineration and distillation, including thermal desorption and hammermill).

Although land treatment is considered among the most acceptable waste disposal methods, it is not without disadvantages. One of the most serious is the increasingly stringent limit on total oil and grease, salts (electrical conductivity) and heavy metals. For land treatment to continue to be a viable disposal option, OBM- and SBM-laden cuttings need to be pre-treated to remove the offensive constituents. Bioremediation is gaining increasing favor in this regard. However, this is considered to be a slow process, and salts and heavy metals are not generally amenable to biodegradation. Nevertheless, bioremediation has been used in several areas, including Western Canada, Venezuela and Southeast United States.

Another approach to improve the environmental acceptability of invert muds has focused on modification of drilling fluid composition. These efforts have concentrated mainly on using alternate synthetic fluids or internal phases. However, problems with reliability and meeting regulatory requirements in a consistent, cost-effective manner have plagued these efforts.

Invert emulsion muds generally contain some components, such as excess lime and clays, that are intrinsically beneficial to many soils.[4] Low pH (< 5.5) is detrimental to most agricultural crops, and often soil needs to be treated with an alkaline material like lime to counteract the effects of low pH. Clays can act as soil conditioners, especially for sandy soil, by improving its texture and increasing its water-holding capacity. In addition, some organics, especially those similar to humus, serve as nutrients and conditioners.

The major components of invert emulsion muds, on the other hand, may not be so beneficial. These include (a) base fluid; (b) emulsifier/surfactant; (d) internal (aqueous or polar) phase; and (e) weighting material. Any one of these may affect seed germination, plant growth and/or the life cycle of native fauna, e.g. earthworms. A typical SBM used on shore is a barite-weighted hydrocarbon-based fluid formulated with a moderate toxicity surfactant package and $CaCl_2$ brine.

In this work, we set out to prepare a new SBM that minimizes environmental impact -- and actually provides needed soil nutrients -- by replacing each of these four major components with environmentally friendly materials, while maintaining the excellent drilling engineering properties for which SBM and OBM are known.

Part of this study also entailed examining bioremediation techniques for pre-treatment of cuttings prior to land spreading or farming in areas of the world where restrictions on discharges are severe.

Experimental Approach

Formulation of a soil-enhancing invert mud required introduction into the mud of environmentally acceptable base fluid, emulsifier package, internal phase and weighting material. For the purpose of this exercise, the mud density was set at 13.0 lb/gal, S/W = 70/30, and the water activity of the internal water phase = 0.86 to 0.76 (equivalent to 18 to 24% CaCl2). Six base fluids; four emulsifier packages; seven chloride-free water soluble materials in the internal phase; two viscosifying organophilic clays; three fluid loss control agents; and three weighting materials were examined.

To minimize the size of the test matrix, toxicity and biodegradability tests were first carried out on the base fluids, and these were used to reduce the choice of base fluid to one. A few preliminary API standard property tests revealed that two of the emulsifier packages would not survive 250°F. Similarly, difficulties with a glycol and concerns with a formate reduced the number of internal phase solutes to five, while initial HTHP performance tests reduced the number of clays and fluid loss control additives (FLCA) each to one; the latter is a nontoxic, relatively inert material. Of the three weighting materials, hematite was chosen immediately for its environmental qualities. Consequently, the initial test matrix of formulations was reduced from 3024 to 10. Naturally, the concentrations of various components (emulsifiers, clay and fluid loss control agents) had to be optimized, and wetting agents were necessary to keep the system together. The nature and concentration of the clay were very critical to the stability of the invert emulsion, and the emulsifier package had to be matched to the nature of the internal phase.

The procedures for mixing the muds and measuring their standard properties are given in Appendix A.

Environmental tests were carried out on the base fluids, several muds, and a few samples of mud-laden cuttings before and after treatment in a bioreactor. The tests, which were conducted at the University of Calgary, consisted of the following:[5] (a) biodegradability (respiration rate and hydrocarbon loss in a reference moist soil); (b) phytotoxicity (alfalfa seed emergence and root elongation); (c) earthworm survival; (d) springtail survival; and (e) Microtox (IC-50 on bioluminescent bacterium *Photobacterium phosporeum*).

Inasmuch as a soil-enhancing invert mud may still meet with regulatory barriers, a complementary effort was made to examine the feasibility of bio-treating mud-laden cuttings beforehand in a bioreactor or via composting.

Results

Mud Composition

Base Fluid. Environmental data on the six base fluid candidates of similar carbon chain length are shown in Tables 1 and 2.

The biodegradability test results displayed in Table 1 do not show any surprises. These indicate that diesel and the branched paraffin are considerably more resistant to rapid biodegradation than the other four fluids. Aromaticity and branching, respectively, are known to reduce biodegradability.[6] The isomerized olefin (tetradecene), or IO, is intermediate in biodegradability, while the two linear paraffins (LP) and the ester exhibit the highest biodegradability.

The toxicity data in Table 2 clearly shows that the diesel and the ester are considerably more toxic than the branched paraffin, LP's or IO in all five tests. The Microtox test also showed some differentiation between the C_{12-13} LP and IO (higher toxicity), and C_{11-14} LP and branched paraffin (lower toxicity). This is to be expected, because higher molecular weight branched fluids tend to exhibit lower acute toxicity in tests that focus on water-column toxicity.

The high toxicity of the ester can be explained with a closer look at its biodegradation behavior. GC-FID analysis of soil extracts from all six fluids shows that the degradation of the ester produces non-volatile intermediate degradation products, including fairly toxic materials like hexanol, 2-ethyl hexanol, 2-ethyl hexanoic acid and 2-ethylhexyl 2-ethylhexanoate. These intermediate products constituted about 30% of the ester lost through biodegradation.

On the basis of the biodegradability and toxicity results, the C_{11-14} linear paraffin was chosen as the base fluid for the remainder of the studies.

Weighting Material. Hematite was chosen over barite and calcium carbonate based on standard mud properties and environmental effects. Ilmenite ($FeO \cdot TiO_2$), though not included in this study, is a potential alternative weighting material. A very large amount of $CaCO_3$ is required for a 13-lb/gal mud, which results in a very high rheology. Barite was not selected as the preferred weight material, because it was not anticipated to provide any beneficial attributes to the final byproduct. Hematite, though more abrasive and apt to produce staining, is an attractive choice, since the toxicity of dissolved iron is generally considered low for most forms of life. Hematite has the potential to provide iron to ironpoor soils and appears to fit the model for product selection.

Internal Phase and Emulsifier Package. The performance of emulsifiers in invert muds is affected by the nature of the base fluid, organophilic clay and internal phase. This requires that the emulsifier package be customized to work well with those components. Various candidate salts and alcohols (including glycols and glycerin) were tested with a number of emulsifier packages before two suitable candidates were identified.

One version of the internal phase is a nitrate brine.[7] A second uses an acetate brine as the internal phase. A third version of the internal phase is a blend of the nitrate and acetate brines. The blend of acetate and nitrate salts was found to be particularly suited for direct land treatment of muddy cuttings, inasmuch as the acetate is intrinsically biodegradable while the nitrate accelerates the overall biodegradation process.

A biodegradable emulsifier was found that could provide good standard mud properties up to at least 250°F. A blend of conventional emulsifiers was also found to be suitable, and it was tested up to 300°F.

Mud Properties

Standard mud properties of three 13-lb/gal, 70/30 (Synthetic/Water ratio) formulations, one with an acetate brine (Formulation A), one with a nitrate/acetate blended brine (Formulation NA) and one with a nitrate brine (Formulation N) are shown in Table 3. A conventional high-performance diesel-based mud with $CaCl_2$ brine internal phase gives standard properties that are very similar. The three formulations in Table 3 were hot-rolled for 16 hr at 300°F, as well as 250°F, with essentially no degradation in rheology or electrical stability (ES).

Biodegradability and toxicity of Formulations A and N are contrasted with those of a typical diesel/$CaCl_2$/barite mud in Table 4. These results show clearly that muds A and N both are consistently more biodegradable and much less toxic than the diesel mud. In comparing Formulation A with a similar formulation weighted with barite (instead of hematite), biodegradability and toxicity appear to be similar for the two muds. However, a soil-enhancing iron source is considered desirable for its long-term potential benefits; consequently, hematite was retained in the formulation.

Except for the Springtail survival data, Formulation A showed consistently lower toxicity than Formulation N. This trend appears to correlate with the trend in electrical conductivity (EC) measured after the biodegradation tests, i.e. after 65 days. Thus, a mud with a higher EC generally gives a higher toxicity, which is to be expected, i.e. toxicity increases with increasing ionic strength. That Formulation A gives such a low EC is thought to be the result of relatively rapid biodegradation of the acetate ion.

The toxicity data for the mud formulations in Table 4 indicate that the % Root Elongation observed for Formulation A is nearly 50% greater than for the control. This suggests that Formulation A may serve to enhance some aspects of the quality of the soil.

Bioremediation

Bioreactor Treatment. The bioreactor procedure used for this work is given in Appendix B. A photograph of two early lab bioreactors is shown in Figure 1.

Simulated drill cuttings thoroughly coated with Formulation N were slurrified and treated in the lab bioreactor at room temperature (25°C). The level of synthetic fluid on cuttings (SOC) was initially about 11% w/w. The results are shown in Figure 2. The biodegradation process exhibits exponential growth as the bacteria population increases. This is manifested in the rapid increase of the Oxygen Uptake Rate (OUR). When the food source (base fluid on the cuttings) depletes to an SOC of about 3% w/w (after about 7 days), the rate of biodegradation peaks and begins to fall rapidly. By 15 days, SOC has fallen to < 1% w/w, and the rate has reached a plateau beyond which little reduction in SOC is observed. By contrast, a conventional diesel-based mud with $CaCl_2$ brine internal phase exhibited a SOC of about 7% w/w even after 21 days.

Ecotoxicity data gathered on bioreactor-treated simulated cuttings are shown in Table 4 for Formulations NA and N. Again, the loading rate on the test soil was 6% w/w. The phytotoxicity results indicate that both sets of cuttings, when pre-treated in the bioreactor, can promote germination and growth of alfalfa seeds. As is the case for the muds themselves (see Table 4 again), bioreactor-treated cuttings appear to enhance the quality of the soil.

As part of the effort to optimize the bioreactor process, temperature was found to be a key factor. Indeed, increasing the temperature by approximately 10°C (to 35°C) cuts the time required for OUR to drop to near-baseline levels (and SOC < 1% w/w) by half, as shown in Figure 3. Little appears to be gained by going beyond 35°C, and above 40°C, hydrocarbon-metabolizing bacteria begin to lose activity.

As crucial as the operating temperature is, efficient transport of oxygen and the presence of other nutrients are equally critical to efficient operation of a bioreactor. Modifying the flow of air to ensure higher and more homogeneous values of Dissolved Oxygen increased the biodegradation rate. Of the muds tested, Formulation N produced the fastest biodegradation rates, indicating the important role that nitrate can play in the degradation process. Spiking the mixture with a general-purpose fertilizer (containing potassium and phosphate along with nitrate) produced similarly enhanced biodegradation rates, and maintaining a high fertilizer content produced the fastest rates of all.

Composting. Details of the composting method are described in Appendix C. A photograph of the rotary composting vessel is shown in Figure 4.

During composting, heat generated by microbial decomposition is retained within the pile, and degradation of the material occurs in a number of distinct phases according to the dominant types of bacteria at any given time. The pile is initially colonized by mesophilic organisms that grow best at ambient temperatures, but as the material degrades and heat builds up in the pile/vessel (usually rising to 50°C within two to three days) they are superseded by thermophilic organisms that thrive at high temperatures (50-60°C). These higher temperatures are more favorable for rapid biodegradation and are used in some compost systems to kill potentially harmful pathogens in a process somewhat akin to pasteurization. As only thermotolerant organisms can survive at the higher temperatures, the microbial numbers start to decline and the composting material cools. At this stage anaerobic conditions may develop, unless sufficient air is introduced. In the third stage, the material continues to cool and the microorganisms compete for the remaining organic material, leading to a breakdown of cellulose and lignins etc. During the final, maturation stage, levels of microbial activity continue to decline as the remaining food is used up and the microorganisms die off.[8]

Results from the initial rotary composting experiment (Figure 5) show a clear reduction in the hydrocarbon content of the composted cuttings over a period of 42 days and show signs of the life cycle described above. As the initial proof of concept studies originally contained relatively low amounts of muddy cuttings, continued investigation of composting is currently being carried out to evaluate the optimum cuttings and hydrocarbon limits, as well as ways in which to speed up the process.

Conclusions

The invert emulsion drilling fluid described in this paper possesses the excellent drilling properties of conventional invert muds but generates drilled cuttings that can be used as a soil-enhancing by-product.

One version of this drilling fluid is expected to undergo relatively rapid natural biodegradation when landspread or farmed and may find use in areas where restrictions on initial discharges are moderate. For areas where regulations severely restrict organic and ionic discharges, two bioremediation techniques – bioreactors and composting – show considerable promise for reducing those discharges to acceptable levels.

Nomenclature

ES = Electrical Stability (API RP 13B-2), V
GC-FID = Gas Chromatograph with Flame Ionization Detector
HTHP = High Temperature, High Pressure
OUR = Oxygen Uptake Rate, mg/L/min
SOC = Synthetic Fluid on Dried Cuttings, % w/w

Acknowledgments

The authors thank M-I*LLC* for permission to publish this paper.

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Appendix A – Drilling Fluid Mixing & Testing Procedure

In all cases, the muds were mixed with a Hamilton Beach (HB) mixer over a period of 1 hr, and then exposed to high shear with a Silverson mixer set at 7000 rpm until the slurry reached 150°F. Property measurements consisted of initial API Electrical Stability (ES) and API standard rheology at 150°F. After heat-aging (rolling) the muds for 16 hr at 250°F, ES, rheology (again at 150°F) and API standard HTHP fluid loss at 250°F were measured.

The best formulations were subjected to more rigorous testing, including prolonged stability at 300°F and resistance to contamination: drilled solids (35 lb/bbl OCMA Clay), seawater (10% v/v) and weighting material (increase of density from 13 to 15 lb/gal). For these tests, four lab bbl of base mud were mixed over a period of 1 hr on the Silverson at 7000 rpm, maintaining the temperature at or below 150°F. To each of three of the lab bbls, one of the contaminants was added and mixed in with the HB mixer for 10 min. As before, intial ES and rheology measurements were followed by heat-aging at

250°F for 16 hr, then ES and rheology (at 150°F) and HTHP fluid loss at 250°F on half of a lab bbl. The other half of a lab bbl of each sample was heat-aged at 300°F for an additional 16 hr, and again ES, rheology (at 150°F) and HTHP fluid loss (at 300°F) were determined.

Appendix B – Bioreactor Test Procedure
The bioreactor treatment is designed to provide accelerated aerobic biodegradation in a controlled environment, and generally involves slurrification of the biodegradable waste. Simulated soil is mixed with the drilling fluid to produce muddy "cuttings", dispersed in a large quantity of water, spiked with a bacterium designed to metabolize hydrocarbons, and the entire slurry aerated continuously with air. The biodegradation rate is determined from measurements of Dissolved Oxygen (DO) and Oxygen Uptake Rate (OUR).

- Formulate 4.5 kg of simulated cuttings consisting of 1/3 Texas bentonite, 1/3 Rev Dust and 1/3 Blast Sand #5 (70-140 mesh).
- Spike the cuttings with 1125 mL (1755 g) of mud.
- Add 10 L of aged tap water into the bioreactor, an inverted 5-gal water bottle with the bottom cut out.
- Add 10 g of bacteria / L (~150g).
- Slurry 900 g spiked soil with 10 L de-chlorinated tap water initially, add 900 g on day 2 and 1800 g on day 4 for a total concentration of about 3600 g/ 15 L or about 240 g/L (24% solids).
- Provide vigorous aeration with aeration device that can provide up to 60 L/min of air.
- Conduct standard API retort analysis of cuttings to determine oil content on solids at beginning and end of test.
- Conduct solvent extraction to determine oil content at the beginning and end of the test for comparison with retort analysis.
- Determine OUR approximately once a day from measurements of Dissolved Oxygen, using a Dissolved Oxygen meter.
- Once a week check pH and maintain in 6 - 9 range.
- Periodically check nitrogen, along with other potential nutrients.
- Continue running the retort for 30 days or until OUR drops to a negligible level.
- Optimize bioreactor performance: temperature, quantity of mud-laden cuttings, air transfer and nutrient levels. Check performance on field cuttings.

Appendix C – Composting Test Procedure
Whereas bioreactor treatment is generally a fluid process (slurrification of solid or liquid biodegradable material), composting usually involves only solids. Windrowing (mechanical or manual turning of the material) and forced aeration of static biopiles are the more common methods, although there are also methods of mixing and aerating the material based on rotating reactors,[8] the method used in our lab tests. The rotary composting vessel has a small footprint and can be used to continuously process the cuttings waste stream. The mixing imparted by the gradual rotation of the drum (0.5 rpm) is enough to ensure adequate aeration of the composting mixture. Use of an insulated drum improves heat retention of the composting mixture and increases the rate of degradation.

Muddy drilled cuttings are mixed together with another solid organic substance that is also reasonably readily degraded, e.g. straw or wood chips. This mixture is usually supplemented with nitrogen, phosphorous and possibly other organic nutrients.[9] Preliminary proof of concept experiments contained a relatively low concentration of drill cuttings (Oxford Shale 5-10 mm diameter) coated with 10% w/w drilling fluid (Formulation N), 40% moisture content, and a carbon to nitrogen ratio of approximately 30:1.[10] Naturally-occuring bacteria were used for these tests.

Table 1
Biodegradability of Various Base Fluids

Treatment	% Reduction of Hydrocarbons	Biodegradability Rank
C_{11-14} LP	97	1
C_{12-13} LP	94	2
Ester	91	3
Isomerized Tetradecene C_{14} (IO)	83	4
Diesel	61	5
Branched Paraffin	43	6

Table 2
Toxicity of Various Base Fluids*

Treatment	Water Toxicity	Animal Toxicity	Alfalfa Phytotoxicity*		Toxicity Rank
	Microtox IC_{50}	% Earthworm Survival	% Seed Emergence	% Root Elongation	
Branched Paraffin	106	100	95	107	1
C_{11-14} LP	98.5	100	96	134	2
C_{12-13} LP	65.9	100	95	120	3
Isomerized Tetradecene C_{14} (IO)	61.7	100	101	144	4
Diesel	10.3	0	7	2	5
Ester	5.9	0	0	0	6

* Seed Emergence and Root Elongation test results are normalized to Control test values of 100.

Table 3
Standard Properties of two Paraffin-Based Fluids

Component (g)	Formulation A		Formulation NA		Formulation N	
Linear Paraffin	144		144		144	
Organophilic Clay	5		5		5	
Lime	3		3		3	
Fluid Loss Reducing Agent	5		5		5	
Emulsifier #1	8		8		8	
Emulsifier #2	2		2		2	
Acetate Brine	97		-		-	
Nitrate/Acetate Brine	-		115		-	
Nitrate Brine	-		-		113	
Hematite	283		267		264	
Rheology at 150° F	**Initial**	**Hot-Rolled***	**Initial**	**Hot-Rolled***	**Initial**	**Hot-Rolled***
600 rpm	55	50	61	51	52	42
300 rpm	31	28	39	30	30	23
200 rpm	24	22	31	22	21	15
100 rpm	15	14	21	14	15	10
6 rpm	6	5	9	5	6	4
3 rpm	5	4	8	4	5	3
PV (cP)	24	22	22	21	22	19
YP (lb/100 ft^2)	7	6	17	9	8	4
10-sec Gel	6	6	8	6	6	5
10-min Gel	9	7	10	6	6	5
Electrical Stability (v)	171	199	320	263	314	242
Internal Phase Water Acti vity	0.86		0.76		0.77	
HTHP Filtrate at 250°F (mL)	-	1.8 est.	-	2.0	-	0.8
Filtrate Water (mL)		trace		Nil		Nil

* Hot-Rolled for 16 hr at 250 °F

Table 4
Biodegradability , Toxicity & Electrical Conductivity of Formulations and Treated Cuttings
6% w/w Loading on Topsoil from Southern Alberta Grassland

System	Biodegrad-ability (65 days)	Animal Toxicity		Alfalfa Phytotoxicity*			Relative Electrical Conductivity (after 65 days
	% Loss of Extractable Hydro-carbons	% Springtail Survival	% Earthworm Survival	% Seed Emergence	% Root Elongation	% Shoot Mass	
Formulation A	98	80	100	100	149	97	1.0
Formulation N	98	87	93	4	11	47	4.0
Std. Diesel / $CaCl_2$ / Barite Formulation	68	0	0	3	8	25	4.9
Formulation A with Barite	99	90	100	100	108	105	0.8
Bioreactor-Treated Cuttings, Form. NA	-	93	100	109	134	129	-
Bioreactor-Treated Cuttings, Form. N	-	73	100	113	116	121	-

*Phytotoxicity test results are normalized to Control test values of 100.

Fig. 1 – Four 15-L Bioreactors

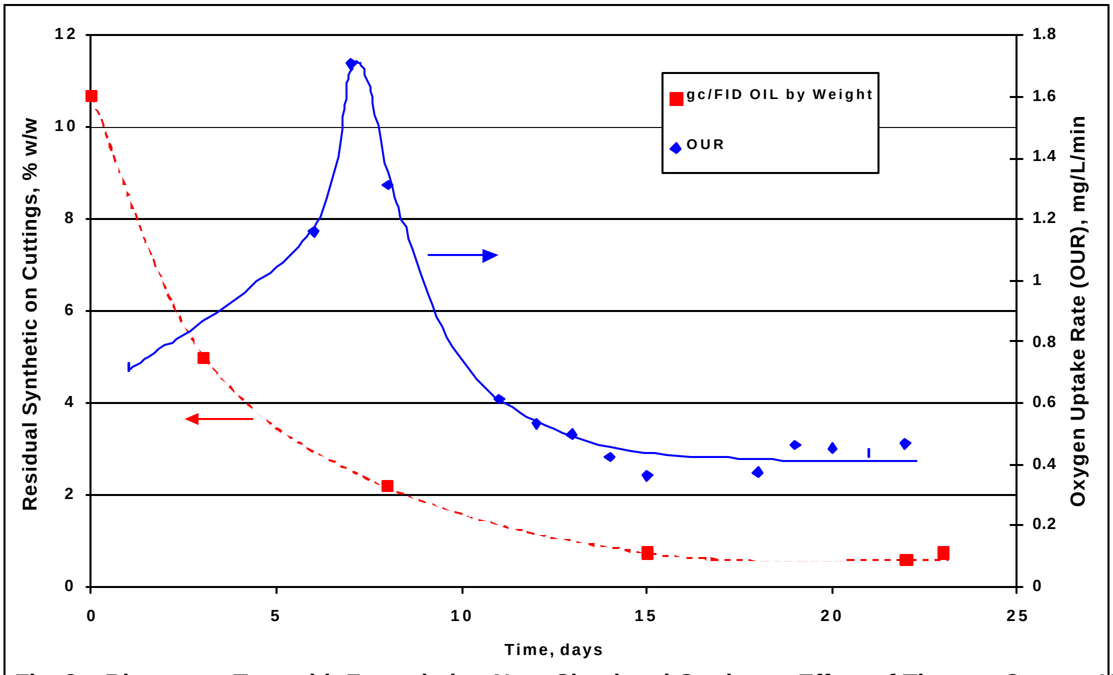

Fig. 2 - Bioreactor Test with Formulation N on Simulated Cuttings: Effect of Time on Oxygen Uptake Rate (OUR) and % Synthetic on Cuttings, 25 °C

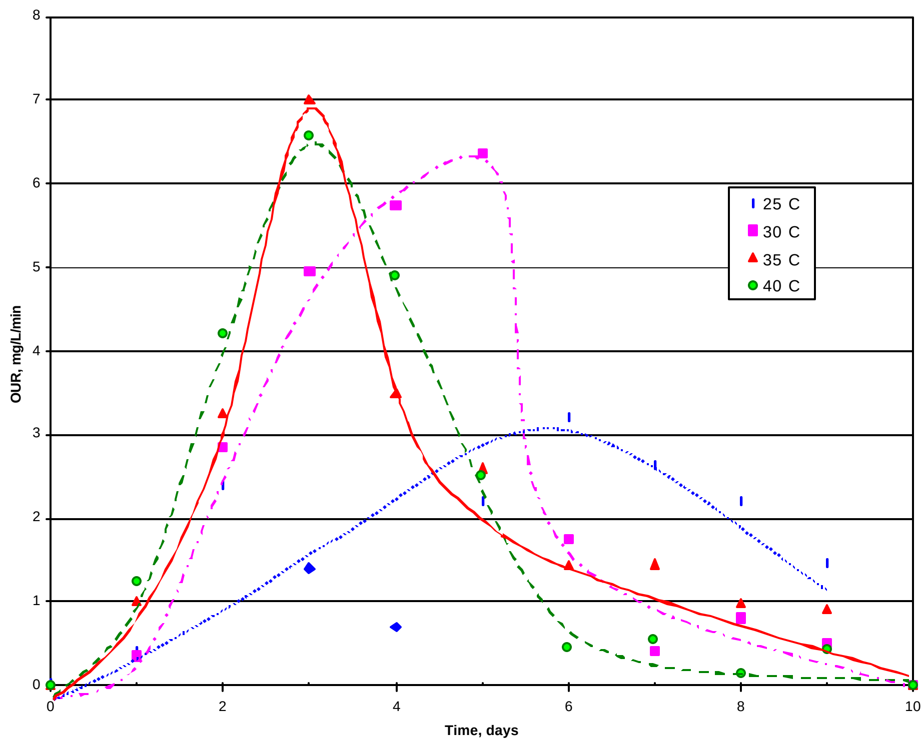

Fig. 3 - Effect of Temperature on Biodegradation Rate in Bioreactor: Formulation N on Simulated Cuttings.

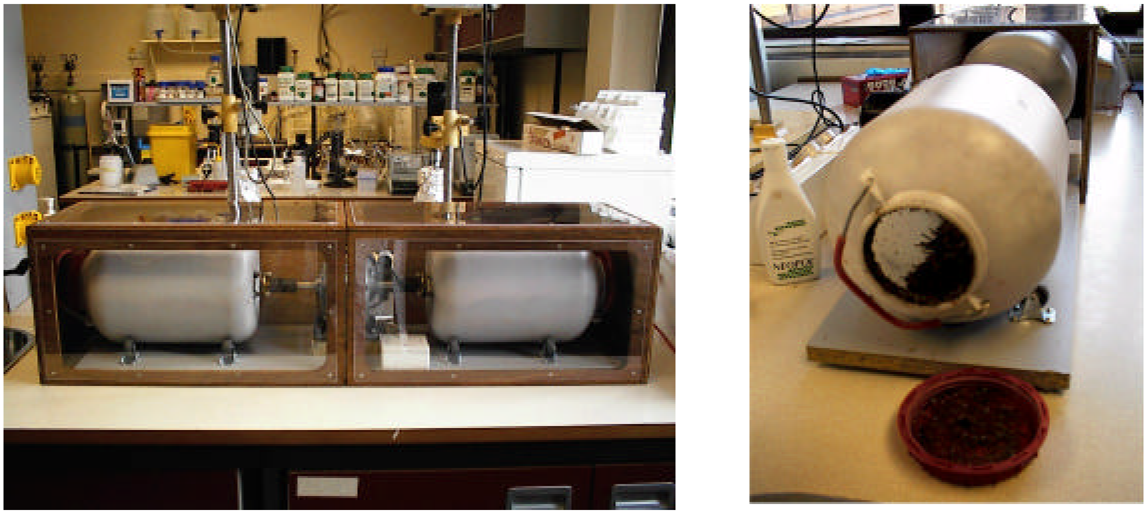

Fig. 4 – Lab scale rotary composter showing encased rotating drums on the left and individual 5-gal drum on the right.

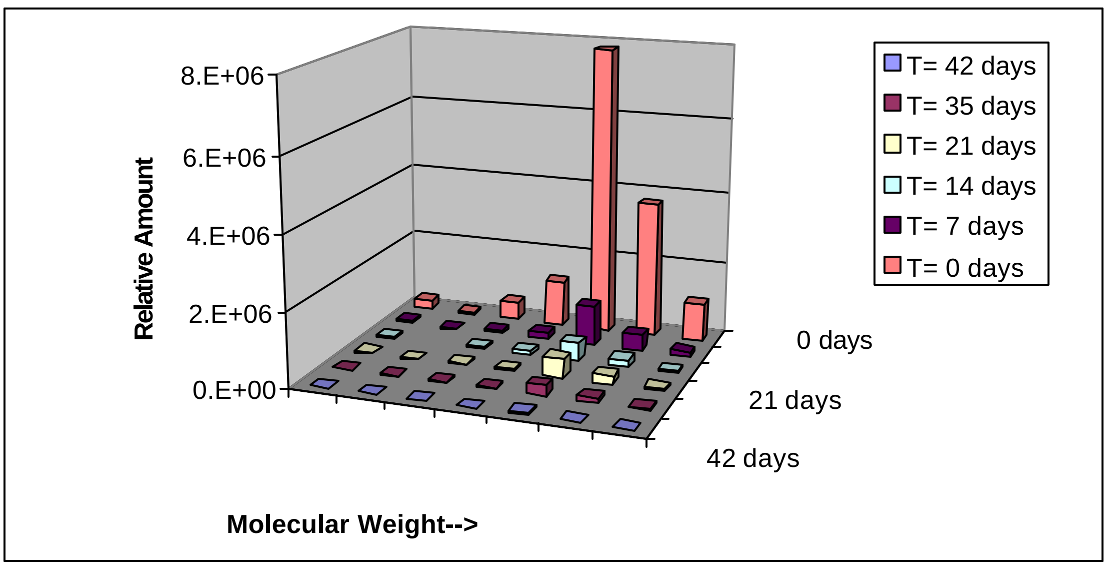

Fig. 5 – Composting trial showing chromatographic analysis of hydrocarbon content of cuttings over a period of 42 days (the seven groups of bars correspond to seven individual components)